

Improvement Of Quality Of The Hydropurified Diesel Fuel By Ion-Liquid Extraction

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Abstract

The article presents the results of the investigations carried out on the improvement of the quality of hydrotreated diesel fuel (HDF) by the method of extraction of ionic liquid on the basis of N-methylpyrrolidone and acetic acid. Influence of various factors – the components ratio, temperature and duration of extraction has been studied on the yield and degree of purification, in particular on the degree of dearomatization and desulfurization of HDF.

It has been found out that in the case of realization of selective purification of HDF by ionic liquid at 3:1 ratio of ionic liquid to feedstock, contact time of the components – 3 hrs, extraction temperature 60, residual aromatics in the raffinate amounts to 4% wt., but sulfur-containing compounds – 0.0153 % wt. Wherein, cetane number amounts to 52.

Practically, complete dearomatization of the feedstock is got at extraction temperature – 20-25, mass ratio of ionic-liquid compound to the feedstock – 2:1 and the components contact time – 1 h. In above-mentioned conditions of extraction, residual content of sulfur-containing compounds in the raffinate, obtained with 88% of yield amounts to 0.0130% wt. Cetane number of purified HDF amounts to 52.

Due to the properties – kinematic viscosity, cetane number and simultaneously residual content of aromatic hydrocarbons, HDF after selective purification by the ionic liquid composition, meets the requirements of Euro-5.

Keywords: *hydropurified diesel fuel, ionic liquid, extraction, cetane number, extragent, raffinate*

Introduction

A development of the oil-refining industry is the strategic task of the domestic economy. The indices growth of the oil industry is mainly determined both

by depth of the oil-refining and by quality of the produced oil products, especially motor fuels.

Among all types of the oil products a special place is occupied by fuel for diesel engines, without which it is impossible to imagine a modern civilization [1].

Now an increase of quality of the diesel fuels is reached basically with use of hydrogenization processes. However, a use of the expensive catalysts, large hydrogen consumption, hard conditions of the process – high partial pressure and temperature, low volume feeding rate of raw materials leading to large investments and specific power inputs during hydropurification and hydrorefinement are the disadvantages of these processes. Consequently, the development of alternative methods of increase of quality of the diesel fuels is the actual task of petrochemistry and oil-refining.

The extraction refinement processes of the diesel fuels allowing to reduce the content of sulphur, nitrogen and polycycloarenes in 5-10 times and considerably to increase the cetane index are perspective [2, 3].

A search of the effective extragents or extraction systems possessing both selectivity and ecological compatibility for refinement of the diesel fuels due to their structural-group composition, a development of approaches and combined methods allowing to increase the selectivity of removal of undesirable components is the perspective and actual problem of petrochemistry and oil-refining.

In this aspect, the so-called ionic liquids, corresponding to the requirements of "green chemistry" and providing the development of new ecologically safe technologies of organic and petrochemical synthesis, as well as oil refining deserve attention. The increased interest to the ionic liquids has been stipulated by complex inherent physical-chemical properties, such as: thermal and chemical stability, non-volatility and

incombustibility, low vapor pressure, ecological compatibility, and also high dissolving capacity of many inorganic, organic and high-molecular compounds of the various composition.

Owing to the listed properties the ionic liquids are successfully used as the catalysts or components in the composition of the catalytic systems, as the monomers for synthesis of ion-liquid polymers or plasticizing agents of high-molecular compounds [4-8] and as the selective solvents in the liquid-phase extraction process [9-14]. The interest to the ionic liquids as extragents in the selective purification processes along with above-mentioned physical-chemical properties has been also stipulated by possibility of their regeneration and recycling, which is one of the main requirements, presenting to the selective solvents.

The prospectivity of application of the ionic liquids as the selective solvents in the selective purification processes of the oil fractions found its confirmation in the results of the systematic investigations carried out at IPCP of Azerbaijan National Academy of Sciences [15-19].

In particular, the possibility of preparation of the diesel fuel corresponding technical requirement presenting to the fuel of class «EVRO-2000» by a method of selective purification of the corresponding distillate with use of ion-liquid extragents on the basis of formic acid and morpholine (or aniline) has been shown [20].

In this paper, the results of the investigations on selective purification of the hydropurified diesel fuel (HDF) by ionic liquid on the basis of N-methylpyrrolidone and acetic acid synthesized by interaction of the components at molar ratio 1:1, at temperature 60°C and reaction time duration for 3 h are presented [21].

Experimental

HDF produced by the oil refinery plant named after H.Aliyev was used as a raw material in the carried out investigations. The hydropurification has been carried out at temperature 340°C, pressure 4 MPa, raw materials feeding rate 1 h⁻¹, hydrogen consumption 350 l/l with use of AGKO-400BH as the catalyst. The prepared HDF characterized by the following fraction composition and physical-chemical indices (table 1).

Table 1. Physical-chemical indices of HDF

Indices	Values
Fraction composition, °C	
P.A.	185
5%	207
10%	220
20%	237
30%	254
40%	265
50%	275
60%	288
70%	301
80%	317
90%	336
96%	362
K.K	364
Density, at 20, kg/m ³	845,7
Refractive index, n _D ²⁰	1,4698
Content of aromatic hydrocarbons, % mass	16
Sulphur content, % mass	0,0181
Congelation temperature, °C	minus 31,8
Flash temperature in closed crucible, °C	75,8
Kinematic viscosity mm ² /s, at 20°C	3,40
Cetane number	47

The experiments on selective purification of HDF were carried out in a three-neck flask equipped with a mechanical stirrer, reflux condenser and thermometer with intensive mixing of the components. At the end of mixing the settling of the prepared mixture was carried out, as a result of which the disintegration of purified raffinate from extract solution consisting of ionic liquid and aromatic and sulfur compounds, as well as resin products removed from the HDF composition occurred.

It has been shown by study of influence of the various factors – ratio of components, temperature and extraction duration that a yield and degree of purification of the diesel fuel is determined both by quantity of extragent in relation to raw material and by extraction temperature. In particular, at temperature 60°C and contact time of the components (3 h) with increase of ratio of IL to raw material from 1:1 w.p. to 3:1 w.p. a yield of the raffinate is decreased from 88,8% to 73,2% mass. In this case, a degree of dearomatization of the initial diesel fuel is vibrated within the range of 62,5-75,0 % mass at residual aromatics content in the purified

distillate by defined method of sulphurization (GOST 6994-74) – 4-6% mass. A residual content of the sulphur-containing compounds in prepared raffinate is 0,0125-0,0153 % mass at their concentration in the initial distillate 0,0181% mass. The cetane number of the purified distillate of HDF is slightly increased and is 49-52 against 47. (Table 2).

Table 2. Dependence of yield and indices of HDF on conditions of selective purification

(a)

Ratio of IL : HDF	Temperature, °C	Contact time, h	Raffinate yield, mass %	Content of aromatic hydrocarbons, mass %	Sulphur content, ppm
1:1	60	3	88,8	6	0.0125
2:1	60	3	81,3	4	0.0141
3:1	60	3	73,2	4	0.0153
1:1	23	3	89,0	7	0.0146
2:1	23	3	82,0	3	0.0135
2:1	23	1	80,5	0	0.0130
2:1	23	0,5	79,6	0	0.0151

(b)

d_4^{20} kg/m ³	n_D^{20}	Kinematic viscosity, mm ² /s	Cetane number
838	1,4659	5,35	49
-	1,4634	5,53	-
829	1,46154	5,8	52
836	1,46390	5,237	50
832	1,46330	5,404	51
831	1,46160	5,400	52
832	1,46150	5,340	51

In a case of carrying out of the selective purification process of HDF distillate stage-by-stage with use of new portion of the ionic liquid

at each stage, at ratio of IL and raw materials 1.5 : 1 w.p., contact time of the components – 90 min. at each stage and extraction temperature – 60°C, a yield of the raffinate is slightly decreased and at the first stage is 80% mass., and the second – 70.4% mass in relation to the raw material. After two-stage purification the residual aromatics content in the prepared raffinate was 4% mass, and sulphur-containing compounds – 0,0127% mass. As is seen, a stage-by-stage extraction favors more deep purification of the fuel (~ 29,83% mass) from sulphur-containing compounds. It has been shown that with decrease of extraction temperature to 20-25°C, a yield of the raffinate is practically not changed and in twofold excess of extragent and contact time of the components (3 h) it is observed a decrease of the residual aromatics content and sulphur-containing compounds in the purified raffinate, which was 3% mass and 0,0135% mass, respectively.

It has been established by investigation of influence of contact time of the components at indicated temperature on degree of purification of HDF and on qualitative indices of the prepared raffinate that at ratio of IL and raw materials 2:1 w.p. a contact time of the components (1 h) a complete dearomatization of raw materials is observed. A quantity of the sulphur-containing compounds in the raffinate is 0,0130 % mass, and cetane number – 52. It has been shown that at contact time of the components (30 min.) at the same conditions of extraction a complete dearomatization of HDF is observed and residual quantity of the sulphur-containing compounds is 0,0151% mass. Thus, by carried out cycle of the investigations on selective purification of HDF by ionic liquid on the basis of N-methylpyrrolidone and acetic acid it has been established the decrease of the raffinate yield and also relatively high residual content of the aromatic and sulphur-containing compounds and time of hydrocarbons in purposeful product and carrying out of the extraction process by temperature rise, a

quantity of extragent and contact time of the components. The best results are reached during carrying out of the process in the conditions of twofold excess of IL, temperature from extraction 25°C and contact time of the components (60 min.). In this case, the raffinate prepared with yield 79,6% is characterized by absence of the aromatic hydrocarbons and residual content of sulphur-containing compounds 0,0130% mass. The cetane number of the purified distillate is 52. As is seen, the diesel fuel after selective purification by this ionic liquid composition on a series of indices – kinematic viscosity, cetane number and on residual content of polycyclic aromatic hydrocarbons meets the requirements Euro-5, and on sulphur content in two times exceeds the standards Euro-3.

The comparative characteristics of diesel distillate before and after selective purification by ion-liquid extragent have been presented in Table 3.

Table 3. Characteristics of the diesel fuel before and after purification by ion-liquid composition

Index name	Diesel fuel		
	before purify-cation	after purification	
		at 60°C	at 20-25°C
Density at 20, kg/m ³ , d ₄ ²⁰	845,7	829	831
Refractive index, n _D ²⁰	1,4698	1,4635	1,4616
Content of aromatic hydrocarbons, % mass	16	4	0
Sulphur content, % mass	0,0181	0,0153	0,0130
Kinematic viscosity, m ² /s	5,39	5,8	5,4
Cetane number	43,5	52	51

It is necessary to add that at ion-liquid extraction the resinous compounds are also removed from distillate, as a result of which the raffinate gets transparent color and is characterized by relatively low refractive index

$n_D^{20}=1,4616$ against $n_D^{20}=1,4698$ of the initial distillate.

Due to the fact that one of the main requirements presenting to the selective solvents used as extragent is the possibility of their regeneration and recycling, we have also investigated the conditions of isolation of the ion-liquid extragent from extract solution. With this aim the prepared extract solution was treated by water. In this case, the ionic liquid was separated from extract phase and then after removal of water by distillation was recycled in the extraction process of DF with the same selectivity.

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